

Estimation of lifetimes of solvent radical cations in liquid alkanes using the level crossing spectroscopy technique

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Abstract

The technique of radical ion pair level crossing spectroscopy was employed to obtain the electron spin resonance spectrum parameters of solvent radical cations for a series of linear nonviscous alkanes (pentane to hexadecane) at room temperature. The spectra consist of a single homogeneous line that becomes broader as the carbon chain of the alkane molecule becomes shorter. Effective hyperfine interactions in radical cations are negligible. The lower estimates for the lifetimes of radical cations were obtained. Assuming that the contribution of spin relaxation to the line width is not important, the lower estimates increase from 1 to 33 ns in the sequence C₅–C₁₆. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

One of the most important unstable intermediates in the radiation chemistry of alkane solutions are the primary radical cations, or holes, of the solvent. Forming in the processes of energy deposit in the medium, they strongly determine the directions and yields of radiation chemical transformations in solution. Although solvent radical cations bear spin, in natural conditions (in liquid solutions at ambient temperature) they cannot be studied by traditional spin-sensitive techniques (electron spin resonance (ESR) and its modifications) due to their short lifetimes. A characteristic time scale is ~ 10 ns, which is much shorter than the period of the Larmor

precession of a spin in the microwave field of a typical ESR spectrometer (~ 100 ns for H_1 of ~ 1 G).

To date, the main body of information about solvent radical cations is still being obtained from time-resolved experiments on optical absorption [1] and electrical conductivity of irradiated solutions [2,3]. Although these techniques have sufficient time resolution, their nonselectivity complicates the interpretation of results. Alkane radical cations have broad structureless optical absorption spectra often superimposed on the absorption bands of other species present in the solution. Separation of the hole contribution to sample conductivity is rather straightforward only when their mobility significantly exceeds that of molecular ions, as in the case of cyclic alkanes [4] or very viscous branched alkane squalane [5].

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In the present work, another spin-sensitive technique, the level crossing spectroscopy of spin-correlated radical ion pairs (MARY spectroscopy), was employed to study solvent radical cations of nonviscous linear alkanes at room temperature.

2. Brief summary of the technique

The technique is based on the observation that in MARY spectra (dependencies of the recombination fluorescence intensity on external magnetic field) sharp lines, corresponding to crossing of magnetic energy levels of recombining pairs, can arise. The shape and position of the lines are determined by the same parameters as the ESR spectrum of the pair. However, in contrast to ESR spectroscopy, the lines are formed due to spin evolution in the pair driven solely by the hyperfine interaction in the partners which can exceed the maximal attainable microwave field H_1 by 1–2 orders of magnitude. Consequently, the technique allows registration of radical ions with lifetimes as short as 1 ns in a stationary experiment [6].

Under irradiation of alkane solutions radical cations are formed as the partners in the spin-correlated radical ion pairs (solvent hole)⁺/electron[−] [7]. Since electron mobilities in alkane liquids are rather high, geminate recombination of such a pair occurs on a picosecond time scale. Introducing an electron acceptor in the solution extends this time to nanoseconds without destroying spin correlation of the pair, thus providing ample time for spin evolution and allowing to study solvent holes.

Hexafluorobenzene C_6F_6 was taken as a convenient electron acceptor for studying alkane holes. This molecule does not scavenge alkane holes and has a satisfactory quantum yield of fluorescence of $\sim 4\%$ in our experimental conditions. More importantly, the fluorine atoms in the hexafluorobenzene radical anion are equivalent in liquid solutions and have large enough hyperfine couplings ($A = 135$ G [8]) to allow registration of rather short-lived radical cations. As has already been demonstrated, two lines

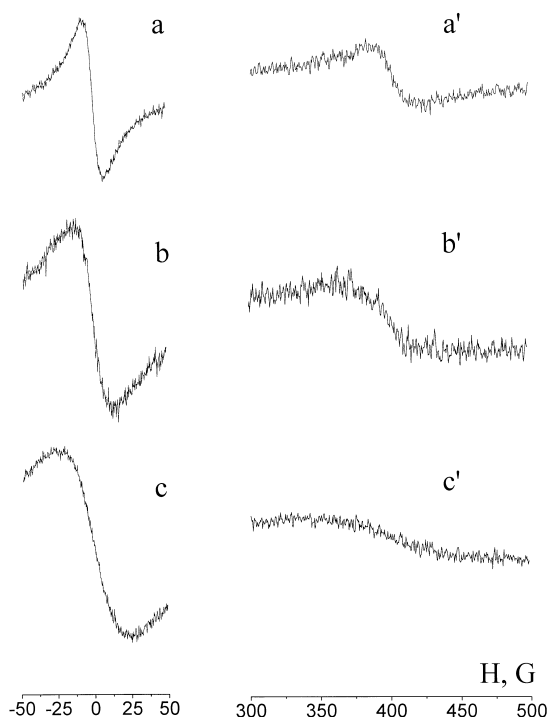
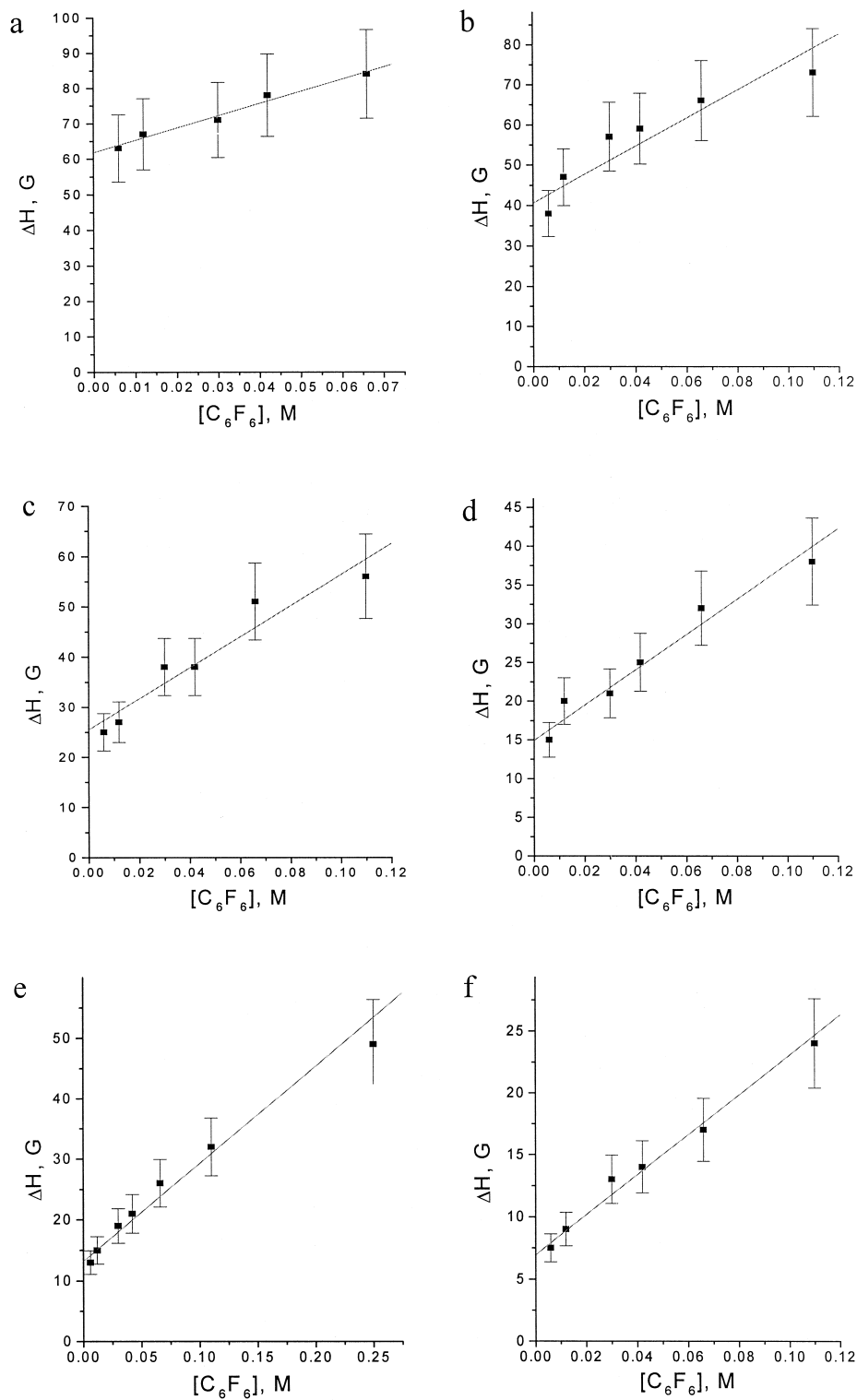


Fig. 1. MARY spectra of the 0.012 M solutions of hexafluorobenzene in dodecane (a, a'), octane (b, b') and hexane (c, c') (a–c, at zero field; a'–c', in the field $H = 3 A = 405$ G).

in the fields $H = 0$ and $H = 3 A = 405$ G are observed in MARY spectra of the pairs with hexafluorobenzene radical anion [9]. The 'homogeneous' contribution (due to the finite lifetime of the correlated pair because of recombination, relaxation, monomolecular decay of the partners, etc.) to the width of the line in the 405 G field is three times larger than it is to the width of the line at zero field. The 'inhomogeneous' contribution (unresolved hyperfine structure of the radical cation) leads to additional broadening of the line at 405 G, leaving the width of the line at zero field practically unchanged [10]. Assuming a Lorentzian lineshape, the width of the line at zero field can be converted to the lifetime of spin-correlated pair via the known ESR spectroscopy relation $\tau = (0.66/\Delta H_{pp})$ ns. The technique of level crossing has already been used to study

Fig. 2. Plots of the peak to peak width of the line at zero field vs. the concentration of C_6F_6 (symbols) and their least-squares linear approximations for the solutions of hexafluorobenzene in pentane (a), hexane (b), octane (c), decane (d), dodecane (e), and hexadecane (f).



squalane [11] and isooctane [12–14] in liquid solutions.

3. Experimental

The MARY spectroscopy arrangement has been described in Ref. [6]. About 1 cm³ of degassed solution in a quartz cuvette was put in the field of a Bruker ER-200D ESR spectrometer equipped with an X-ray tube for sample irradiation (Mo, 40 kV $\times$ 40 mA) and a photomultiplier tube to detect fluorescence (FEU-130). The external magnetic field was modulated at a frequency of 12.5 kHz with an amplitude up to 15 G. A Stanford SR-810 Lock-In Amplifier and computer averaging over 10–20 scans were used to get the presented spectra, given as the first derivatives of the actual field dependencies. No microwave power was applied to the samples. All experiments were carried out at room temperature ($20 \pm 2^\circ\text{C}$). The solvents – *n*-pentane, *n*-hexane, *n*-octane, *n*-decane, *n*-dodecane, *n*-hexadecane – were stirred with concentrated sulphuric acid, washed with water, distilled over sodium and passed through a column of activated alumina. Hexafluorobenzene and *p*-terphenyl-*d*₁₄ were used as received.

4. Results and discussion

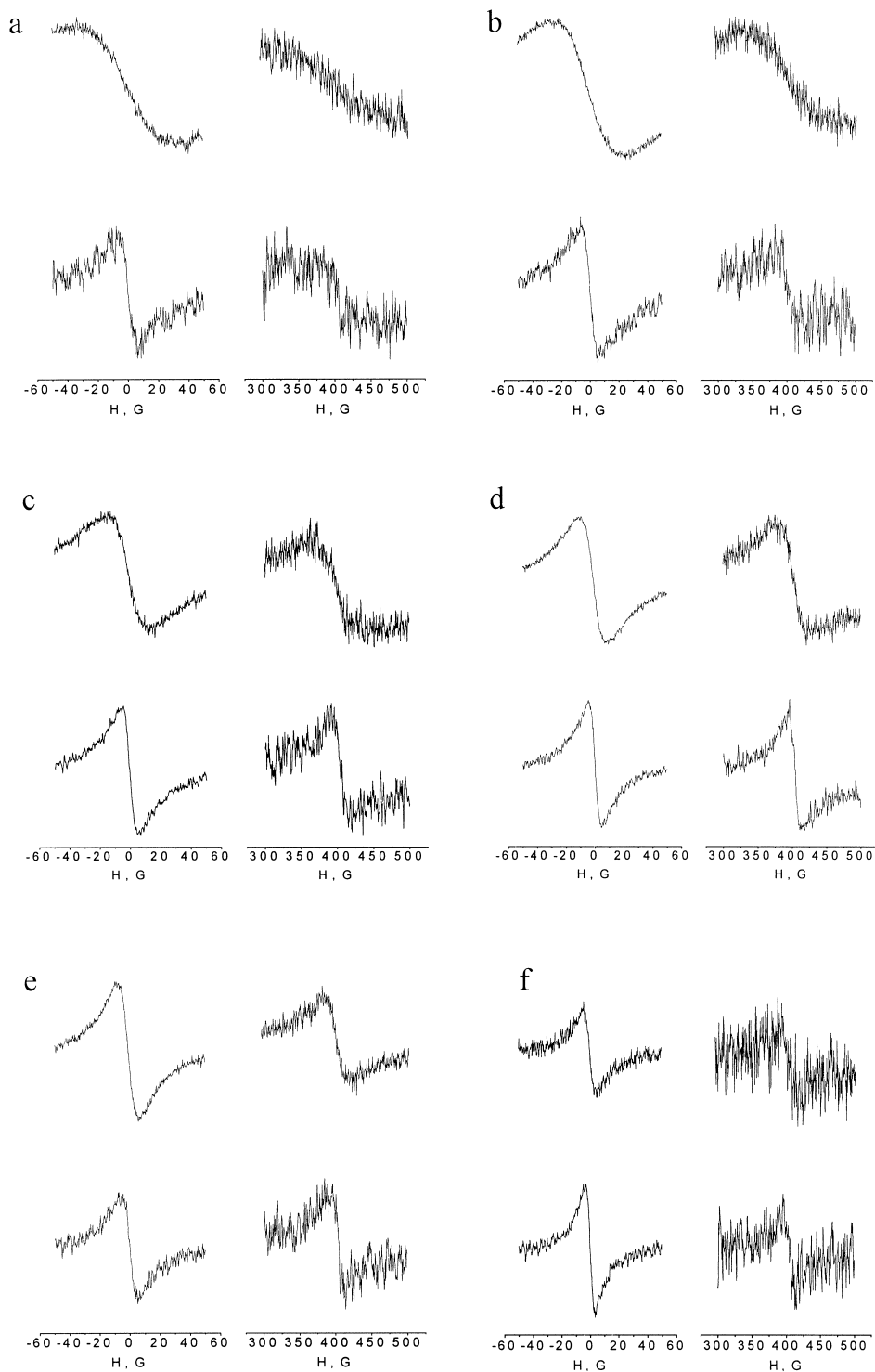
Fig. 1 shows the typical experimentally observed lines at zero field (left) and in the field $H = 405$ G (right) for the solutions of 10^{-2} M C₆F₆ in hexane, octane and dodecane. Similar results were also obtained for the other three alkanes. The presence of the signals indicates that there are recombining spin-correlated radical ion pairs in these systems. The line in the 405 G field shows that one of the pair partners is the hexafluorobenzene radical anion.

Possible candidates for the radical cation partner of the pair are: solvent radical cation, radical cation of an unknown impurity which quickly scavenges the solvent radical cation, or radical cation of an

olefin quickly forming via the monomolecular decay of the solvent radical cation. The ratio of the widths of lines in the fields $H = 405$ G and $H = 0$ is close to 3:1 in all studied systems. Hence there is no appreciable ‘inhomogeneous’ contribution to the width of lines, i.e. the radical cation partner of the pair has negligibly weak effective hyperfine couplings compared to the ‘homogeneous’ line widths. Radical cations of olefins generally have rather broad ESR spectra and the concentration of olefins in the irradiated solutions in our experiments was too low to provide effective charge transfer narrowing of their spectra. As a result, the observed signal cannot be ascribed to an olefin radical cation. The same arguments also hold for the radical cations of impurities. Consequently, the observed MARY spectrum is formed in the pairs C₆F₆^{•−}/(solvent hole)^{•+}. Effective hyperfine couplings in the solvent hole can be rather weak due to charge transfer from holes to abundant neutral solvent molecules and due to the fast conformational motions within the solvent radical cation itself.

Since the lines of MARY spectra appear to be ‘homogeneous’ for our systems, further measurements were performed only for a stronger line at zero field. The processes that contribute to its width include chemical decay and spin relaxation of the solvent hole and relaxation of the hexafluorobenzene radical anion mostly due to charge transfer to a neutral C₆F₆ molecule. Because of a rather large hyperfine coupling constant, the radical anion stays in the region of slow charge transfer for all solvents studied. Here, the charge transfer reaction gives an additive contribution to the linewidths which is proportional to the concentration of C₆F₆ in solution [9] and the widths increase linearly with increasing concentration. Fig. 2 summarises the plots of the widths of lines at zero field vs. C₆F₆ concentration for the six studied alkanes. The slope of the linear fit gives the rate constants for the ion–molecular charge transfer reaction of C₆F₆^{•−} and extrapolation to zero concentration yields contributions to linewidth other than those resulting from electron exchange.

Fig. 3. MARY spectra of the 0.012 M solutions of hexafluorobenzene in pentane (a), hexane (b), octane (c), decane (d), dodecane (e), and hexadecane (f) at zero field (upper left of the subfigure) and in the field $H = 3$ A (upper right) and the analogous spectra after adding 2×10^{-4} M *p*-terphenyl-*d*₁₄ to the solutions (lower left and right).



The reaction rate constants and linewidth contributions at zero field thus obtained, for all studied solvents, are given in Table 1. The accuracy of extracting rate constants from the experimental spectra is $\sim 15\%$. The table also gives rate constants, estimated in the diffusion-controlled limit from the known solvent viscosities. As can be expected, the experimentally obtained rate constant increases with decreasing viscosity. However, it stays significantly below the estimated diffusion-controlled limit, which indicates kinetic control of the reaction of charge transfer from C_6F_6^- to a neutral C_6F_6 molecule in nonviscous alkanes. The difference between two values decreases with increasing viscosity, and in very viscous squalane the measured rate constant is determined by the rate of diffusional collisions [9].

To extract the contributions of finite lifetime and relaxation rates for the solvent hole itself from the line width extrapolated to zero hexafluorobenzene concentration, the hole was substituted for an aromatic radical cation and the changes in the spectra were considered. Experimentally, this was done by adding an effective hole acceptor *p*-terphenyl- d_{14} (PTP) to the solution of C_6F_6 in alkane. Since aromatic hydrocarbon radical cations are rather stable and have quite long relaxation times, up to microseconds, their intrinsic properties do not contribute to the observed 'homogeneous' line widths. The 'inhomogeneous' contribution of the PTP radical cation in the 405 G field is also negligible because of its negligible hyperfine couplings. Furthermore, such a substitute would not significantly

change the diffusional mobility of the radical cations in the studied alkanes and, thus, would not change the kinetics of geminate recombination of pair partners, which can also influence the observed widths.

Fig. 3 shows the transformation of the line at zero field (left-hand columns in subfigures) and in the field $H = 3 \text{ A}$ (right-hand columns) after adding $2 \times 10^{-4} \text{ M}$ PTP to the solutions of 10^{-2} M C_6F_6 in alkanes. Although the relative fraction of pairs with the radical cation of PTP is not large (the characteristic hole scavenging time in these conditions is $\sim 100 \text{ ns}$), a significantly higher quantum yield of fluorescence for PTP and a significantly smaller 'homogeneous' width for pairs $\text{C}_6\text{F}_6^-/\text{PTP}^+$ as compared to $\text{C}_6\text{F}_6^-/\text{hole}^+$ lead to domination of the signal from the former in the experimentally observed spectra. Generally, other conditions being equal, only the narrowest line is observed experimentally.

It can be seen from the figure that substituting the solvent hole for a stable radical cation results in a decrease in the widths of both lines, the decrease being more pronounced for shorter homologues. Since the only difference in the two types of recombining pairs is assumed to be the hole-specific processes shortening the pair lifetime, we conclude that these processes do make an appreciable contribution to the observed width. For example, for pentane this contribution, estimated as the difference between peak to peak widths of the line at zero field, amounts to 53 G.

The data on all studied alkanes are collected in Table 1. As the length of carbon chain increases, the

Table 1
Summary of the characteristics of radical ions in irradiated alkane solutions

Alkane	K_{exch}^a	η/K_{diff}^b	$\Delta H_{\text{total}}^c$	ΔH_{h}^d	τ_{h}^e
C_5H_{12}	5×10^9	$0.24/2.8 \times 10^{10}$	62	53	1
C_6H_{14}	4.5×10^9	$0.31/2.1 \times 10^{10}$	40	35	2
C_8H_{18}	4.5×10^9	$0.54/1.2 \times 10^{10}$	25	14	5
$\text{C}_{10}\text{H}_{22}$	3×10^9	$0.92/7.2 \times 10^9$	15	10	7
$\text{C}_{12}\text{H}_{26}$	2×10^9	$1.35/4.9 \times 10^9$	12	5	13
$\text{C}_{16}\text{H}_{34}$	2×10^9	$3.34/2.0 \times 10^9$	7	2	33

^aRate constant of the ion–molecular charge transfer reaction of the hexafluorobenzene radical anion, $\text{M}^{-1} \text{ s}^{-1}$.

^bAlkane viscosity at room temperature, cP, and estimated diffusion-controlled limit of the charge transfer reaction rate constant, $\text{M}^{-1} \text{ s}^{-1}$.

^cExtrapolated to zero concentration of hexafluorobenzene width of MARY spectrum line at zero field, G.

^dChange in the width of line at zero field, attributed to intrinsic properties of the solvent radical cation itself, G.

^eEstimated from lifetime of the solvent radical cation, ns (lower estimate). Assuming Lorentzian line shape the peak to peak width of the line at zero field is converted to time via the relation $\tau = (0.66/\Delta H_{\text{pp}}) \text{ ns}$.

width of lines monotonically decreases (from tens to units of gauss for the line at zero field). The relative error in the determination of the width is tens of percent and increases with increasing carbon chain length. Assuming that the role of spin relaxation at this time scale can be neglected, the estimated lifetimes of solvent holes change from nanoseconds to tens of nanoseconds.

There are not many numerical data on the lifetimes of radical cations of linear alkanes in the literature. The mechanism of hole decay in a pure solvent (monomolecular decay, reaction with another solvent molecule, e.g. proton transfer, scavenging by an impurity with lower ionisation potential) is also not yet clear and probably is not even unique. A fast component with a decay time of $\sim 10^{-8}$ s, attributed to solvent radical cations, was observed in the optical absorption spectra of hexane and higher homologues [1]. No solvent radical cation band was observed in pentane, presumably due to its fast decay to the pentene radical cation [15]. The values of 5 ns for the lifetime of hexane hole [16] and 37 ns for hexadecane hole [17] appeared in the literature. These observations are in fair agreement with our results.

It should be mentioned that spin relaxation, more specifically the relaxation due to electron exchange, can also contribute to the experimentally obtained widths of the MARY lines of alkane holes. Another possible reason for broader lines can be the contribution from the non-exponential geminate recombination kinetics of radical ion pairs [18], manifestation of which in MARY spectroscopy is not still clear. However, the lifetimes given in Table 1 can be considered to be reasonable lower estimates of the alkane hole lifetimes in ambient conditions.

5. Conclusions

In this work, we have systematically used a spin-sensitive technique, MARY spectroscopy, to obtain for the first time the ESR spectrum parameters of the short-lived solvent radical cations of a series of linear nonviscous alkanes (pentane to hexadecane) in liquid solution at room temperature. The spectra are single lines narrowed by electron exchange, growing broader with shortening carbon chain of alkane. The lower boundary for the lifetimes of holes estimated

from the widths of MARY lines increases from 1 to 33 ns in the sequence C_5 – C_{16} .

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